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COMMONWEALTH OF AUSTRALIA

PATENT SPECIFICATION

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Complete Specification Entitled POLYMERS.

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Related Art: Nil.

The following statement is a full description of this invention, including the best method of performing it known to US :

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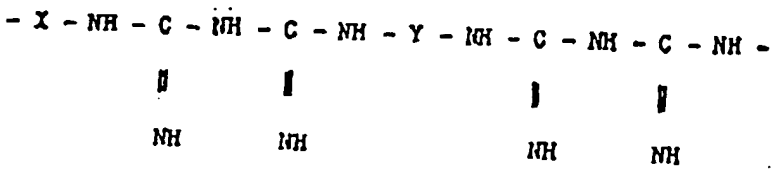
This invention relates to synthetic polymeric material and especially to synthetic polymeric material containing bacteriostatic or bactericidal compounds.

British Patent Specification No. 702,268 describes polymeric substances which in the form of their free bases are linear polymeric substances in which the recurring unit is represented by the formula -



wherein X and Y stand for bridging groups in which together the total number of carbon atoms directly interposed between the adjacent nitrogen atoms is greater than 9 and smaller than 17. Such polymeric substances are referred to hereinafter as polymeric biguanides.

We have found by incorporating the said polymeric biguanides with synthetic polymeric material that bacteriostatic or bactericidal properties are imparted to the synthetic polymeric material.

Thus our invention provides a composition comprising a synthetic polymeric material and a polymeric biguanide as hereinbefore defined.

Synthetic polymeric materials which may be used in the composition of our invention include, among others, polyamides, polyesters and polyolefins. Particularly suitable polyamides are the synthetic linear polyamides known generically as nylons which may be obtained by the polycondensation of aminocarboxylic acids or of diamines with dicarboxylic acids and of which well known examples are polycaprolactam (nylon 6) and polyhexamethylene adipamide (nylon 66). Particularly suitable polyesters are those obtained by polycondensation of dicarboxylic acids or their ester forming derivatives with dihydroxy compounds especially glycols; a well known example is polyethylene terephthalate. Suitable polyolefins include polyethylene and especially polypropylene.

If desired the polymeric biguanide may be used in the form of a salt. Particularly suitable polymeric biguanides are those of the above formula in which X and Y represent chains of methylene groups. An especially suitable example is that in which both X and Y represent hexamethylene, namely polyhexamethylene biguanide, especially in the form of its hydrochloride.

The compositions of our invention may be in any desired form. Thus they may be in powder form or in massive form. Alternatively they may be in the form of shaped articles. Since many of the polymeric materials used in the compositions of our invention, especially polyamides, polyesters and polyolefins, are suitable

for spinning into fibrous form, the compositions may be in fibrous form or in the form of textile materials fabricated from such fibres.

The compositions of our invention may be manufactur d in various ways. Thus the powdered synthetic polymeric material may be mixed with the polymeric biguanide. Alternatively, the synthetic polymeric material in the form of lumps or chip, especially nylon chip, may be coated with the polymeric biguanide by tumbling the chip in a solution of the polymeric biguanide in a solvent, followed by evaporating off the solvent; for example a solution of a salt of the polymeric biguanide in water may be used. Alternatively again the polymeric biguanide may be added to the constituents of the synthetic polymeric material before polymer sation takes place, or may be added at some stage during the polymerisation, and the polymerisation completed. Thus the polymeric biguanide may be added to an aqueous solution of hexamethylenediammonium adipate, which is then subjected to thermal polycondensation with removal of water to give polyhexamethylene adipamide containing the polymeric biguanide, or the polymeric biguanide may be added during the polycondensation. In any case the composition may be melted and fabricated into a shaped article by moulding or extrusion. It is a particular advantage of the compositions of our invention that the bacteriostatic or bactericidal properties are not destroyed by the high temperature required for melting.

Where the compositions of our invention are manufactured by adding the polymeric biguanide to the constituents of the synthetic polymeric material before or during polymerisation, and the operation is carried out in steel vessels it is desirable, in order to avoid corrosion of the vessels that polymeric

biguanide be used in the form of the free base or in the form of a salt with a non-corrosive acid. Particularly suitable salts are the phosphate, the cyclohexylph sphonate and salts with an organic carboxylic acid, especially an aliphatic carboxylic acid, for example the acetate, stearate or adipate. When the synthetic polymeric material is polyhexamethylene adipamide, the adipate is a particularly useful choice, since adipic acid is a constituent of the polymeric material and no extraneous anions are thereby introduced.

The compositions of our invention have bacteriostatic or bactericidal properties. They are active particularly against Gram positive organisms. Compositions of our invention in the form of shaped articles are particularly valuable where the shaped articles are of the kind used in contact with the human body since the growth of bacteria is thereby inhibited. Examples of such shaped articles are textile materials used for clothing or used as gauze or bandages for surgical dressings, or bristles used in hair brushes or tooth brushes.

Compositions of our invention in the form of shaped articles obtained by melting followed by moulding or extrusion are particularly resistant to washing or dry cleaning operations and their bacteriostatic or bactericidal properties are not substantially impaired when the articles are treated by such processes.

Although a wide range of proportions of polymeric biguanide may be used in the compositions of our invention, a very useful range of proportions lies between 0.1 % and 5.0 % by weight. Other materials may also be incorporated, if desired, in the compositions of our invention, for example pigments, fillers, mould release agents, antioxidants, heat stabilisers,

viscosity stabilisers or delustrants.

Th invention is illustrated but not limited by the following Examples in which the parts and percentages are by weight

Example 1

99.5 Parts of polyhexamethylene adipamide chip were agitated in an aqueous solution of 0.5 parts of polyhexamethylene biguanide hydrochloride. The water was evaporated under reduced pressure and drying completed by heating at 80°C for 30 minutes in a vacuum oven. The chip coated polyamide was subsequently spun through a spinnerette at 290°C to produce a yarn which was then drawn 400 %.

The bactericidal properties of the resultant fibres were assessed in the following manner -

0.5 g. samples of the fibres were placed in a distilled water suspension of either Staphylococcus aureus (Gram positive type bacterium). At varying time intervals 1 ml. aliquots were removed and the number of surviving organisms determined by counting. Standard nylon fibres containing no antibacterial agent were used as control. The results are tabulated below and demonstrate the bactericidal properties of these modified nylon against Gram + ve organisms.

		Log_{10} Bacterial Count			
Sample	Bacteria	1 hour	3 hours	7 hours	24 hours
Fibres containing 0.5 % polyhexamethylene biguanide hydrochloride	Staph. aureus	5.289	5.566	2.778	< 1.0
Nylon Control Fibres	Staph. aureus	5.422	4.808	3.580	1.778

Example 2

Samples of polyhexamethylene adipamide, polyethylene terephthalate and polypropylene in the form of chip were coated

with 0.5 % of polyhexamethylene biguanide hydrochloride from aqueous solution by the method described in Example 1. The coated chip was melted and spun into yarn. The bactericidal properties of the yarn were assessed by the method described in Example 1. The results are given in the following table

Synthetic Polymeric Material	Polymeric Biguanide	Log_{10} Bacterial Count : Staphylococcus aureus			
		1 hour	3 hours	7 hours	24 hours
Polyhexamethylene Adipamide	None (Control)	5.422	4.808	3.580	1.778
	0.5 % poly-hexa - methylene biguanide hydro - chloride	5.289	5.566	2.778	1.000
Polyethylene Terephthalate	None (Control)	6.933	6.923	6.785	6.065
	0.5 % poly-hexa - methylene biguanide hydro - chloride	7.103	6.544	5.616	2.644
Polypropylene	None (Control)	6.584	5.380	4.319	3.314
	0.5 % poly-hexa - methylene biguanide hydro - chloride	6.230	3.000	2.653	1.681

Example 3

Polyhexamethylene adipamide yarn containing 0.5 % of polyhexazethylene biguanide hydrochloride prepared as described in Example 1 was woven into a plain weave fabric having 74 picks and 88 ends per inch. The fabric was subjected to bacterial testing as follows -

1 inch square pieces of the test fabric were innoculated with 0.1 ml. of a saline solution containing Staphylococcus Aureus.

After 1 hour the samples were diluted with 10 ml. distilled water and 10 ml. Saline solution and a 0.5 ml. aliquot transferred into nutrient agar. After 24 hours incubation at 37°C the number of surviving organisms was determined by counting. Repeat determinations were carried out at various intervals up to 24 hours. Standard bactericide-free nylon fabric was used as control.

Samples of the fabric which had previously been subjected to five dry cleaning operations were also tested.

The results are given in the following table.

Polyhexamethylene Adipamide Fabric

Polymeric Biguanide	After - treatment of Fabric	Log_{10} Bacterial Count : Staphylococcus Aureus			
		1 hour	4 hours	6 hours	24 hours
None (Control)	-	3.810	3.666	2.950	1.415
	5 X Dry Clean	3.980	-	3.666	1.415
0.5 % poly - hexamethylene biguanide hydrochloride	-	3.291	3.100	2.305	0.301
	5 X Dry Clean	3.948	-	2.665	0.602

Example 4

Polyhexamethylene biguanide base was prepared by passing an approximately 2 % solution of polyhexamethylene biguanide hydrochloride in aqueous methanol down a column containing an ion exchange resin to remove chloride ion, and corporating the effluent from the column to give a pale yellow resin. The acetate, adipate, phosphate, stearate and cyclo-hexylphosphonate salts were prepared by neutralising the base with the appropriate acid. The base requires one equivalent of acid per unit in the polymer chain.

The base or the salt was mixed with polyhexamethylene adipamide chip containing 0.3 % of titanium dioxide and the mixture melted and stirred under nitrogen for 15 to 20 minutes to give an intimate blend and then allowed to solidify. The solid was remelted and spun into yarn. The yarn was scoured and carded to give it a fluffy texture like cotton wool, and samples submitted to bactericidal testing as described in Example 3 except that 0.07 gram samples of the carded yarn were used in place of the 1 inch square samples of fabric. The results are given in the following table.

Polyhexamethylene Adipamide Yarn.

Polymeric Biguanide	Log_{10} Bacterial Count : Staphylococcus Aureus		
	1 hour	6 hours	24 hours
None (Control)	6.40	6.40	5.78
2.0 % Polyhexamethylene biguanide acetate	5.74	5.06	1.30
0.5 % Polyhexamethylene biguanide acetate	-	3.72	2.58
0.5 % Polyhexamethylene biguanide adipate	-	5.18	2.39
0.5 % Polyhexamethylene biguanide base	-	4.05	1.66

Example 5

5,240 parts of hexamethylenediammonium adipate, 6 parts of acetic acid, 9.7 parts of 60 % aqueous hexamethylenediamine, 22.6 parts of polyhexamethylene biguanide base and 2,500 parts of water are gradually heated in a sealed autoclave until the temperature reaches approximately 270°C, the pressure being maintained at a maximum of 250 lbs. per square inch by allowing water to escape as steam through a valve. The resulting molten polyhexamethylene adipamide is discharged from the

autoclave, cooled in water and the resulting s lid broken into chip. The chip is remelt_d and spun into yarn.

Exampl 6

The process of Example 5 is repeated but the 22.6 parts of polyhexamethylene biguanide base are replaced by 18.1 parts of polyhexamethylene biguanide cyclohexylphosphonate.

Example 7

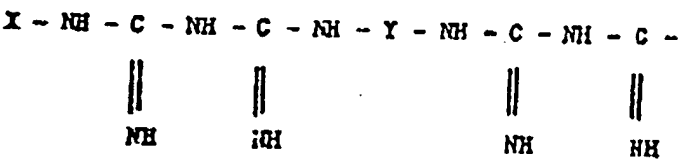
The process of Example 5 is repeated except that the polyhexamethylene biguanide base is added to the autoclave through a pressure lock during the heating period.

Example 8

The process of Example 6 is repeated except that th polyhexamethylene biguanide cyclohexylphosphate is added during the heating period as described in Example 7.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS :

1. A composition comprising a synthetic polymeric material and polymeric biguanide which in the form of its free base is a linear polymeric substence in which the recurring unit is represented by the formula -



wherein X and Y stand for bridging groups in which together the total number of carbon atoms directly interposed between the adjacent nitrogen atoms is greater than 9 and smaller than 17. (23.5.66).

2. A composition as claimed in claim 1 in which the synthetic polymeric material is a polyamide. (23.5.66)

3. A composition as claimed in claim 1 in which the synthetic polymeric material is a polyester. (23.5.66)

4. A composition as claimed in claim 1 in which the synthetic polymeric material is a polyolefin. (23.5.66)

5. A composition as claimed in any of the preceding claims containing from 0.1 % to 5.0 % by weight of the polymeric biguanide. (23.5.66)

6. A composition as claimed in any of the preceding claims in which X and Y in the recurring unit of the polymeric biguanide represent chains of methylene groups. (23.5.66)

7. A composition as claimed in any of the preceding claims in which the polymeric biguanide is polyhexamethylene biguanide. (23.5.66)

8. A composition as claimed in any of the preceding claims in which the polymeric biguanide is used in the form of a salt. (23.5.66)

9. A composition as claimed in any of the preceding claims in the form of a shaped article. (23.5.66)

10. A composition as claimed in claim 9 in fibrous form. (23.5.66)

11. A process for the manufacture of shaped articles as defined in either of claims 9 or 10 which comprises mixing the synthetic polymeric material with the polymeric biguanide, melting the resulting mixture and fabricating the molten composition into a shaped article by moulding or extrusion. (23.5.66)

12. A process for the manufacture of shaped articles as defined in either of claims 9 or 10 which comprises coating the synthetic polymeric material in the form of lumps or chip by tumbling the lumps or chip in a solution of the polymeric biguanide in a solvent followed by evaporating the solvent, melting the coated chip and fabricating the molten composition into a shaped article by moulding or extrusion. (23.5.66)

13. A process for the manufacture of shaped articles as defined in either of claims 9 or 10 which comprises adding the polymeric biguanide to the constituents of the polymeric material before or during the polymerisation, completing the polymerisation, and fabricating the resulting composition in molten form into a shaped article by moulding or extrusion.

14. A process for the manufacture of shaped articles of polyhexamethylene adipamide which comprises the thermal polycondensation of hexamethylenediammonium adipate with removal of water to give polyhexamethylene adipamide, and fabricating the resulting polymer in molten form into a shaped article by moulding or extrusion, in which process a polymeric biguanide as defined in claim 1 is added to the hexamethylenediammonium adipate

or during the polycondensation. 3 - MAY 1967

15. A process as claimed in either of claims 13 or 14 in which the polymeric biguanide is used in the form of the free base, of the cyclohexylphosphonate salt or of a salt with an organic carboxylic acid. 3 - MAY 1967

16. A process as claimed in claim 14 in which the polymeric biguanide is used in the form of the adipate. 3 - MAY 1967

17. A synthetic polymeric material having bacteriostatic or bactericidal properties substantially as herein particularly described especially with reference to the Examples. (23.5.66)

DATED this 8th day of May A.D. 1967

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